Novel Composite Membranes for Hydrogen Separation in Gasification Processes in Vision 21 Plants

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INTRODUCTION

The Vision 21 Program of the Department of Energy is addressing the development of cost-effective power systems that are substantially cleaner and more efficient than systems in use today. Achieving this goal will require the development of both new energy conversion technologies and new generating systems that incorporate this technology. Among these "enabling" technologies are high temperature gas separation membranes, and in particular, membranes that can separate hydrogen from mixed gas streams in a cost-effective manner.

ITN Energy Systems, Inc., along with its partners, the Idaho National Engineering and Environmental Laboratory, Argonne National Laboratory, Nexant Consulting, LLC and Praxair, Inc., are developing composite membranes for the separation of hydrogen from coal gasification streams. The ITN team is pursuing a novel approach to hydrogen separation membrane technology where fundamental engineering material development is fully integrated into monolithic module fabrication designs and manufacturing techniques.

The technology in this program is based on Ion Conducting Ceramic Membranes (ICCM) that remove hydrogen from the gasification streams. Because the membranes are dense, 100% selectivity for hydrogen can be obtained. The membrane process will also result in a stream of concentrated carbon dioxide. This allows for facile separation and capture of this major greenhouse gas.

TECHNICAL APPROACH

The technical approach for achieving the program objectives is three-fold: novel materials development, the integration of materials, module design and fabrication techniques and plant engineering design. The basic building block of the membrane system is a tri-layer consisting of the thin-film, mixed proton and electron conducting membrane and a porous catalyst layer on each side. This structure is illustrated in Figure 1.

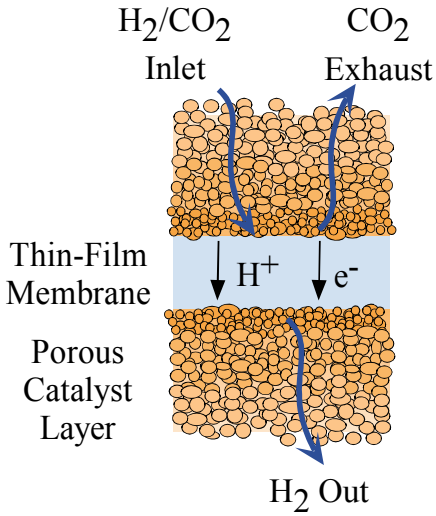

Figure 1. H_2 separation membrane tri-layer assembly.

Materials Development

As illustrated in Figure 1, the H_2 separation membrane needs to conduct both protons and electrons. In this program, the focus is on cermets consisting of a proton conducting ceramic combined with a metal for electrical conductivity. For proton conducting materials, previous work has focused primarily on rare-earth-doped strontium cerate, strontium zirconate and barium cerate.[1-8] These materials have high ionic conductivities, ~10^{-2} S/cm at 600-800°C. However, they are poor electrical conductors, precluding their use in H_2 separation membranes.

Recently, Balachandran and co-workers at Argonne National Laboratory have developed cermet membranes utilizing strontium and barium cerates as the proton conducting phase and with nickel as the electron conducting phase.[9,10] They reported quite high H_2 flux rates, $9x10^{-2}$ $cm^3/min\text{-}cm^2$, at 750°C with relatively thick membranes, ~0.5mm. Since the flux rate is inversely proportional to the membrane thickness, commercially attractive flux rates could be achieved with membranes of thickness on the order of tens of microns.

One major concern of membranes comprised of strontium and barium cerates is their chemical stability. Specifically, barium oxide, and to a lesser extent, strontium oxide, react with both water and carbon dioxide, major components of Vision 21 process streams, to form hydroxides and carbonates, respectively. This reaction is less of a problem at high temperatures but still can be the deleterious to membrane chemical and mechanical stability during the membrane fabrication process and during membrane module start-up and shut-down procedures.

To overcome this problem with membrane reactivity, ITN is developing alternate proton conductors that are based on pyrochlore phases with little or no barium or strontium content. Pyrochlore phases are attractive for this application for several reasons. Recent work has pointed to specific pyrochlore phases that exhibit proton conductivity.[11-13] The pyrochlore crystal structure is based on the fluorite structure with additional oxygen vacancies that promote proton conductivity. The fluorite structure typically shows high chemical and mechanical stability and this high stability is not expected to be degraded by the presence of additional oxygen vacancies. As an example, the well-known oxide conductor, yttria-stabilized zirconia, crystallizes in the fluorite structure. In this program, ITN is developing new materials by rationally doping the base pyrochlore materials. The goal is to obtain materials which exhibit high ionic conductivity and maintain high chemical and mechanical stability.

Module Design and Fabrication

In addition to membrane materials development, ITN is also focusing in this program on techniques for preparing multi-membrane modules. Here, it is necessary to consider the mechanical properties, such as strength and thermal expansion, in order to properly design a multi-membrane module. Additionally, the design must take into account potential manufacturing techniques that are inexpensive and scalable.

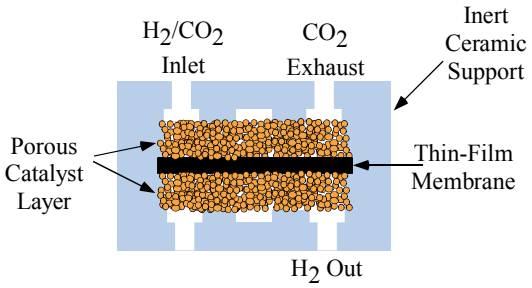

Figure 2. Schematic illustration of a single membrane unit.

Figure 2 shows a schematic illustration of single membrane unit. The membrane/catalyst tri-layer is embedded in a housing which serves as

manifolding for the gas inlets and outlets. The main issue in this approach will be matching the coefficients of thermal expansion for the membrane housing and membrane tri-layer assembly. To make the single cell unit, three fabrication schemes are being developed. The first scheme is to fabricate the tri-layer assembly separate from the housing using conventional ceramic component fabrication processes and subsequently join it to the housing using advanced metallization techniques. Alternatively, the membrane tri-layer and housing can be fabricated in a single unit using thermal spray techniques. Finally, the third fabrication scheme will be some combination of the other two processes.

Once the single cell membrane unit is fabricated, a monolithic, multi-membrane module can be fabricated by joining the individual together the individual single cell units. This is illustrated in Figure 3. Again, advanced metallization techniques can be applied to form the single cell units into a monolithic module.

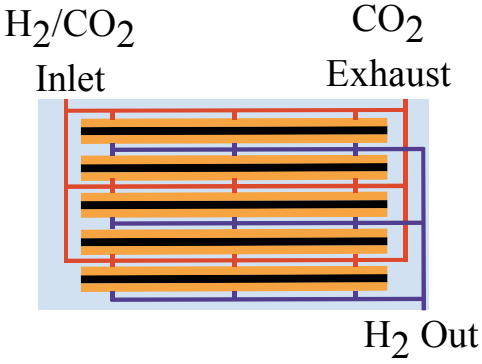

Figure 3. Monolithic, multi-membrane H_2 separation module.

Plant Engineering Design

The required membrane performance specifications are strongly tied to overall plant design and economics. As part of the program, a plant design using ITN's enabling H_2 separation technology will be compared to a baseline plant design using existing H_2 removal technologies (*i.e.* pressure swing adsorption). This will highlight the utility of the membrane technology. A second goal is to compare configurations with performance and costs in the context of the Vision 21 plant vs. current technology.

For this program, several process flow diagrams are being developed. These process flow diagrams are divided into subcomponents such as the air separation unit and power train. These subcomponents take into account both 2002 and 2010 technologies. A matrix of various process scenarios is being developed that will allow for performance and cost comparisons between the process flow diagrams.

EXPERIMENTAL WORK AND RESULTS

Materials Development

Approximately twenty, doped pyrochlore materials have been identified as potential proton conductors. Initial attempts were made to synthesize these materials using conventional solid state techniques. Specifically, powders of the appropriate metal oxides in the proper stoichiometry were ball-milled and subsequently fired at 1200^{o}C. The resulting powders were then analyzed by x-ray diffraction (XRD) and found to be multi-phased due to incomplete reaction. The powders were then re-fired several times at temperatures as high as 1600^{o}C. Based on the XRD results, it was found that phase pure materials could not be prepared, even at the highest temperatures. This high-temperature processing also resulted in very coarse powders. Attempts to prepare sintered cermet membranes from these powders resulted in membranes with densities typically below 80% of theoretical. Membranes with such low densities are not acceptable because they will likely contain connected-through porosity that enables gas phase

diffusion of H_2 and CO_2. This would dramatically lower selectivity, making the membrane unacceptable for Vision 21 applications.

The literature indicates that the identified materials can be prepared single-phased. Therefore, it appears that the problem was one of incomplete reaction, despite the high reaction temperatures. One way to achieve complete reaction is to fire the materials at even higher temperatures or longer times. However, this will result in powders with large particle size which in turn will make it difficult to achieve a high density membrane. This was already observed for membrane using powders sintered at 1600°C.

An alternate, low-temperature powder preparation technique was chosen to overcome this processing problem. After reviewing the literature on low-temperature powder preparation techniques, the well-known Pechini method was chosen.[14-16] This method is suitable for the preparation of complex metal oxide powders, yields powders with very fine particle size at low temperatures and should be readily scalable for producing large quantities of powders that will be required for low-cost fabrication.

The Pechini method starts with an aqueous mixture of metal salts, typically as nitrates. A gel is formed from this solution through the polymerization reaction between citric acid and ethylene glycol. The resulting gel is then fired at relatively low temperatures, 700-900°C, to yield a fine, homogenous, powder of the desired metal oxide formulation.

Several doped pyrochlores have been prepared using powders synthesized from this method. Figure 4 shows the XRD pattern of one particular sample. The pattern shows no reflections due to any of the constituent metal oxides indicating that it is single-phased. Additionally, the broad reflections are indicative of a very fine powder.

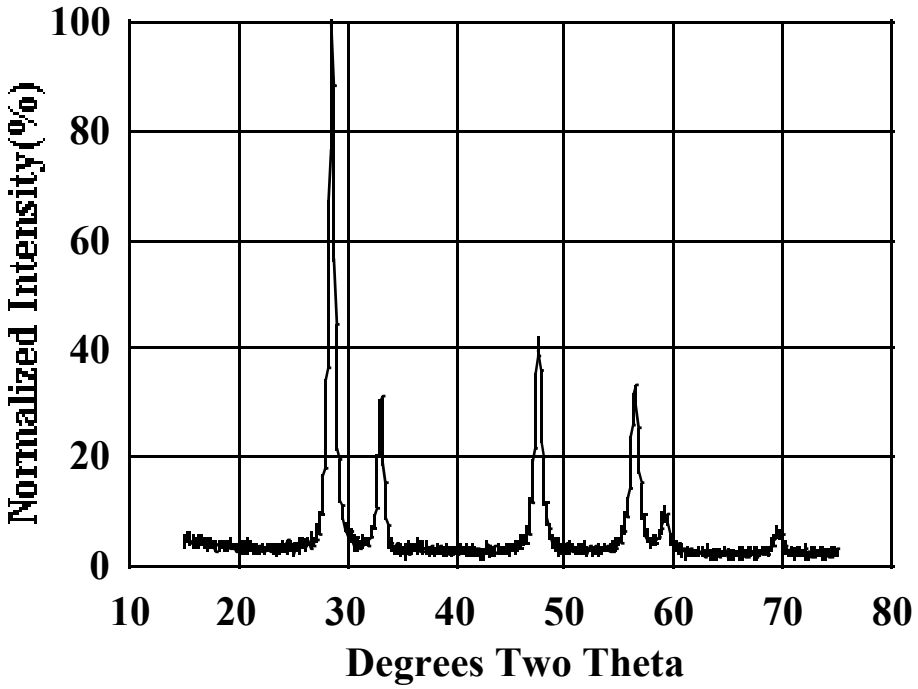

Figure 4. XRD pattern of a doped pyrochlore prepared using the Pechini process.

Membrane Fabrication

Powders prepared by the Pechini method were subsequently fabricated into cermet membrane disks by uniaxial pressing. The general procedures are as follows. Ceramic powders prepared as described above were ball-milled with Ni powder (Cerac, <1μm). An aqueous binder solution (2wt% polyvinyl alcohol) was added and the resulting slurry dried in air. The dried mixture was then passed through a 300μm sieve, placed in a cylindrical die and then pressed uniaxially. The resulting membrane disks were then fired at 300°C in air for binder burnout followed by sintering at 1400-1450°C in 3% H_2 in Ar. Membranes prepared in this manner were typically >90% dense. An example is shown in Figure 5. Samples prepared in this manner are currently undergoing testing.

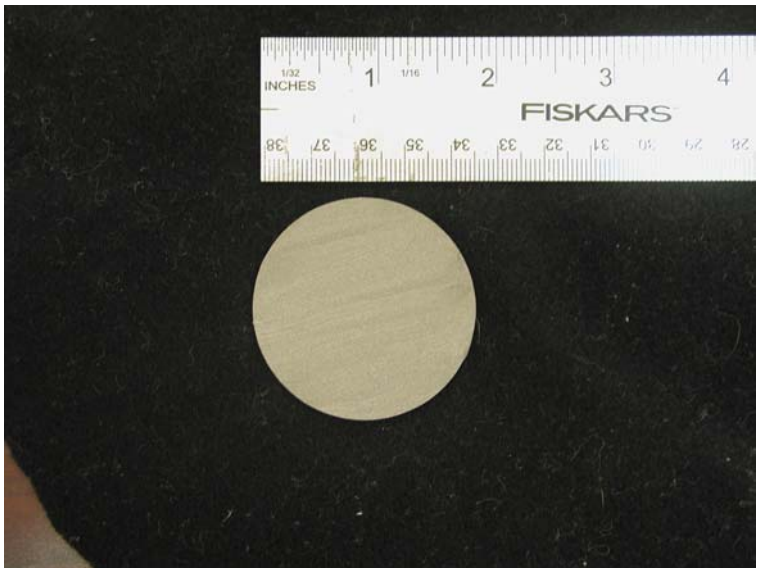

Figure 5. Photograph of a cermet membrane consisting of a pyrochlore proton conducting ceramic and nickel.

CONCLUSIONS

ITN is developing novel cermet membranes for H_2 separation in future Vision 21 power plants. The work involves the development of novel materials, development of techniques for the fabrication of multi-membrane modules and preparing and evaluating plant designs incorporating the novel membranes. ITN has identified novel membrane materials and has successfully prepared cermet membranes incorporating these novel materials. These cermet membranes are currently being evaluated as to their performance as H_2 separation membranes.

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